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THE DECOMPOSITION OF SURROGATE FUEL MOLECULES DURING COMBUSTION

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SUMMARY AND OVERVIEW: This project is aimed at developing a chemical kinetic database consisting of the rate constants of fundamental single step reactions that describe the pyrolytic decomposition of surrogate fuels molecules. These reactions represent an integral part of any complete combustion kinetics database. They can be competitive with oxidation processes and hence extend the range of current combustion models to richer mixtures. They lead to the unsaturated fragments that are the inputs to PAH/SOOT models and are therefore necessary for the use of such models for the description of particle formation with realistic fuels.

TECHNICAL DISCUSSION: This project began on February 1, 2006. Work that is being reported here are therefore of a preliminary nature. Our first task was to obtain a series of compounds that can be used as precursors for the formation of the various radicals of interest. A number of compounds have now been obtained and studies have been initiated.

Surrogate fuel mixtures contain compounds that have structural features that are the same as found in real fuels. The type of compounds include linear alkanes, branched alkanes, branched

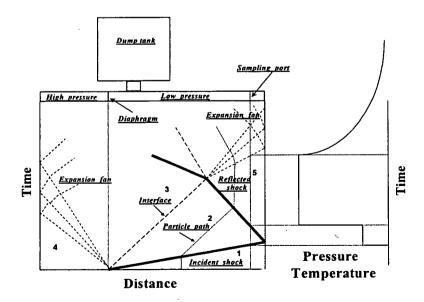


Figure 1: Schematic of single pulse shock tube and associated wave diagrams.

$$C_3 H_6 + iC_3 H_7 \longrightarrow C_3 H_6 + H$$

$$C_3 H_6 + nC_3 H_7 \longrightarrow C_2 H_4 + CH_5$$

$$C_2 H_4 + iC_4 H_9 \longrightarrow C_3 H_6 + CH_5$$

$$iC_4 H_8 + C_2 H_5 \longrightarrow C_2 H_4 + H_5$$

Figure 2: Mechanism for the decomposition of 4-methylpentyl radical. The olefins are those detected from the gas chromatographic analysis.

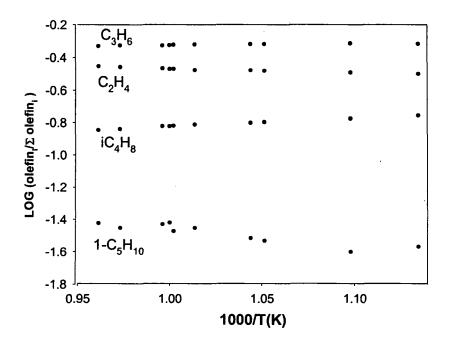


Figure 3: Olefin distribution as a function of temperature from the decomposition of 4-methylpentyl-1 radicals from single pulse shock tube experiments at approximately 3 bar.

cyclanes, and branch aromatics. In a combustion system these compounds are converted into radicals. The radicals can be oxidized or be pyrolyzed. Much of the existing work on combustion models have focused on oxidative degradation. However pyrolytic decomposition is the

competitive process and is usually neglected. This is the justification for the present work. It is expected that when combined with oxidative models it will be possible to extend the models to richer situations. The products from pyrolytic decompositions are the precusors to SOOT/PAH models and hence relates sooting tendencies to the fuel.

Our initial interest is to extend our past work on linear alkanes to cover branched alkanes. Hence we begin our studies on the decomposition of 4-methyl-pentyl iodide in single pulse shock tube experiments. Figure 1 is a schematic of our experimental configuration. The decomposition of the iodide leads to the formation of 4-methylpentyl-1 radical. The results will be compared with earlier results on the decomposition of 1-pentyl radical. Our primary interest will be the effect of methyl substitution on 1-4 isomerization processes. We have detected all the expected products from the decomposition process. They are ethylene, propene, isobutene and 1-pentene. The specific reaction processes are in Figure 2. The branching ratios in terms of olefin yields can be seen in Figure 3. We are in the process of analyzing the results in terms of the specific rate

Figure 4: Mechanism for the decomposition and interconversion of 1-hexenyl-6 and cyclohexyl radicals.

constants. As in the case of the normal alkyl radicals we will begin by deriving rate constants for beta bond scission from experiments on related molecules. This well involve direct studies as well as results derived from the rate constants of the reverse radical addition process. The added features from this study are the effects of methyl substitution for 1-4 isomerization and the consequences of changing an exothermic 1-5 hydrogen transfer from a primary to a secondary position to a thermally neutral process involving primary hydrogen atoms. Systematic studies of this type should lead to the construction of a library of rate constant for hydrogen transfer isomerization in alkyl radicals. A major problem in deriving such data is the difficulties in obtaining the requisite precursors. The 4-methyl pentyl iodide was a custom synthesized sample and cost \$3000.00 for 10 grams. Fortunately one of the great advantages of single pulse

shock tube studies is the need for very small samples. We will therefore wait for the analysis of the results before carrying out further studies aimed at discerning the methyl substitution effect for 1-5 hydrogen transfer isomerization in 5-methyl-hexyl radical as derived from the iodide.

We have also carried out preliminary experiments for the decomposition of 1-hexenyl-6 and cyclohexyl radicals. The 1-olefinyl radicals are formed from the 1-olefins that are in turn derived from the decomposition of alkyl radicals. Their decomposition leads to the formation of dienes. These are known to be very important soot precursors. The overall mechanism is very complex and can be seen in Figure 4. There are three isomerization pathways superimposed on beta bond scissions. Previous lower temperature experiments on cyclohexyl radicals have established the relative stability of the cyclic structures (cyclohexyl and cyclopentylmethyl) in comparison to the linear 1-hexenyl-6 radical. In our experiments we see extensive butadiene formation. This is indicative of the more important role of the linear structure at the higher temperatures. In combination with the earlier work, it should now be possible to describe in a quantitative manner the rate constants of the reactions in Figure 4. These results are also of interest in that they shed light on the decomposition of cyclohexyl radicals. This is the result of radical attack on cyclohexane. Cyclohexane type compounds are important components of tar sands. The latter are expected to form increasingly important component of fuel mixtures. Information on their combustion and sooting behavior is expected to be important in the simulation of these new fuels.